

ADVENTITIOUS CARBON ON PRIMARY SAMPLE CONTAINMENT METAL SURFACES.

M. J. Calaway¹ and M. D. Fries². ¹ Jacobs, NASA Johnson Space Center, Houston, TX; ² NASA, NASA Johnson Space Center, Astromaterials Acquisition and Curation Office, Houston, TX; michael.calaway@nasa.gov.

Introduction: Future missions that return astromaterials with trace carbonaceous signatures will require strict protocols for reducing and controlling terrestrial carbon contamination. Adventitious carbon (AC) on primary sample containers and related hardware is an important source of that contamination. AC is a thin film layer or heterogeneously dispersed carbonaceous material that naturally accrues from the environment on the surface of atmospheric exposed metal parts [1-3].

To test basic cleaning techniques for AC control, metal surfaces commonly used for flight hardware and curating astromaterials at JSC were cleaned using a basic cleaning protocol and characterized for AC residue. Two electropolished stainless steel 316L (SS-316L) and two Al 6061 (Al-6061) test coupons (2.5 cm diameter by 0.3 cm thick) were subjected to precision cleaning in the JSC Genesis ISO class 4 cleanroom Precision Cleaning Laboratory. Afterwards, the samples were analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

Precision Cleaning: All four test coupons were cleaned using the following procedure with ultrapure water (UPW) at 18.18 M Ω -cm and < 5 ppb TOC:

- Degrease with Brulin 815GD added to UPW; polyester wipe mechanical scrub and 15 min. soak
- UPW 40°C rinse, 1 min.
- Ultrasonication 72kHz UPW bath, 30 min.
- UPW 40°C Rinse, 2 min.
- Isopropanol alcohol (IPA) rinse, 30 sec.
- UPW 40°C Final Rinse, 1 min.
- Liquid particle counts on final rinse
- Gaseous nitrogen dry

After cleaning and drying, the samples were packaged face-to-face and wrapped three times in baked-out, UV-O₃ exposed aluminum foil. UPW liquid particle counts on all coupons were taken on a Particle Measuring Systems LiQuilaz E15; channels set at 2, 5, 10, 15, 25, 125 μ m particle sizes. The determination of Particle Cleanliness Class IEST-STD-CC1246E (2013) formula was used and found that all test coupons were at or below the UPW background: < Level 20 at < 22 particles/100 ml at 2 μ m size.

XPS Results: A PHI Quantum 2000 with a Monochromated Al α 1486.6eV X-ray source was used for XPS analyses. The analysis area was 0.14 x 0.03 cm with a surface depth of ~ 5 to 10 nm. The surface composition of SS-316L and Al-6061 coupons are reported in atomic percent (at%) and calculated weight percent (wt%) in fig. 1.

The Al-6061 surface was primarily Al, O, and C with low to trace levels of F, Mg, N, Si, P, and Cl (fig. 1). The carbon was found to be 12.8 at% with hydrocarbon C–C, C–H bonds predominating (fig. 2). Smaller peak intensities were also found for C–O, C–N, and O–C=O species. These rather low carbon levels are attributable to adventitious species [4]. Al and O were found at binding energies consistent with the oxide layer, Al₂O₃. Si was found as silicone and/or silicate. N was found as organic species. F and Cl were found as inorganic halides and P was found as phosphate.

| Element | Al-6061 | | SS-316L | |
|---------|---------|------|---------|------|
| | at% | wt% | at% | wt% |
| C | 12.8 | 8.5 | 20.4 | 11.7 |
| N | 0.3 | 0.2 | 1.4 | 0.9 |
| O | 61.0 | 53.9 | 58.3 | 44.6 |
| F | 2.8 | 2.9 | 0.5 | 0.5 |
| Mg | 1.0 | 1.3 | ND | ND |
| Al | 20.6 | 30.7 | ND | ND |
| Si | 0.7 | 1.1 | ND | ND |
| P | 0.7 | 1.2 | 7.4 | 11.0 |
| Cl | 0.1 | 0.2 | ND | ND |
| Cr | ND | ND | 4.3 | 10.7 |
| Fe | ND | ND | 7.5 | 20.0 |
| Cu | ND | ND | 0.2 | 0.6 |
| | 100% | 100% | 100% | 100% |

Fig. 1: XPS results in at% and calculated wt% (ND: Not Detected)

The SS-316L coupon surface was primarily C, O, P, Cr, and Fe with low to trace levels of N, F, and Cu (fig.1). In addition, Ni was possibly observed near the detection limit. The carbon was found to be 20.4 at% with hydrocarbon C–C and C–H bonds having the primary signal (fig. 3). Smaller peaks intensities were also found for C–O, C–N, and O–C=O species. While SS-316L has higher C levels compared to the Al-6061, this is still within the range of adventitious species. Fe and Cr were found primarily as oxides/hydroxides with low to trace amounts of FeO and CrO. The Cr/Fe ratio was < 1 which is unusual for electropolished stainless steel [5]. Trace amounts of Cu was found as CuO. N was found as organic species and P was found as phosphate. A trace amount of F was found as a combination of inorganic and organic species.

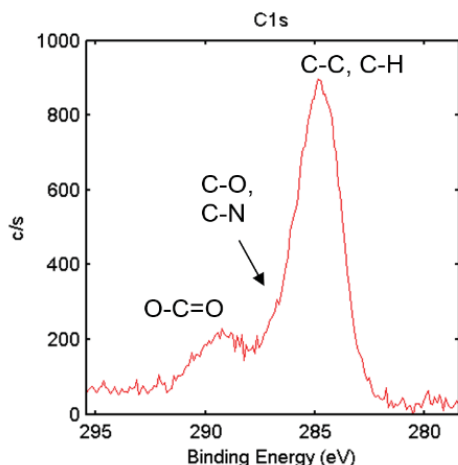


Fig. 2: Al-6061 XPS C1s Peaks at 284.8, 286, and 288.5 eV

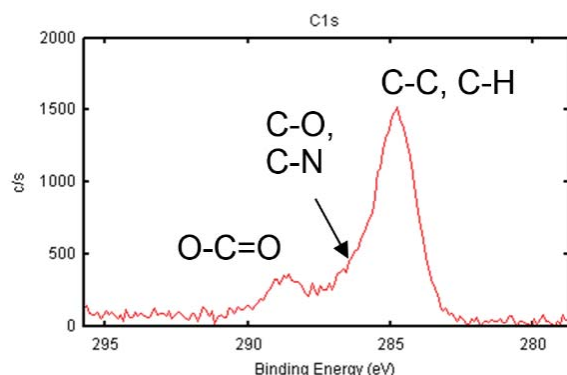


Fig. 3: SS-316L XPS C1s Peaks at 284.8, 286, and 288.5 eV

Raman Spectroscopy Results: The measurements were performed using a Horiba LabRam instrument for qualitative identification of organic surface species for comparison with XPS bulk chemistry results.

The Al-6061 coupon surface spectra were dominated by the D and G bands (1350 and 1580 cm^{-1}) for elemental sp^2 bonded disordered carbon. The band at $\sim 2660\text{ cm}^{-1}$ was also indicative of sp^2 bonded carbon and the signal at $\sim 2920\text{ cm}^{-1}$ is possibly due to a combination of D and G bands as well as from hydrocarbons. The Tuinstra-Koenig relation was used to calculate the grain size $L_a(\text{\AA})$ of graphitic carbon: $L_a(\text{\AA}) = 44 \times (\text{IG/ID})$, where ID and IG are the D and G band intensities (peak areas). This calculation yielded a macromolecular carbon crystallite grain size of $2.1 \pm 0.2\text{ nm}$ on the surface of the Al-6061.

The SS-316L surface resulted in no detection of sp^2 carbon or hydrocarbons. A found piece of debris did result in a very weak signal with peaks at 1360 and 1620 cm^{-1} , however, additional surface particles analyzed also showed no evidence of carbon or hydrocarbons.

Discussion: Adventitious carbon contamination is typically found by XPS on metal surfaces between 40-60 at% [1, 4]. Al_2O_3 (native oxide) on Al is typically ~ 28 at% C and Cr_2O_3 on stainless steel is ~ 44 at% C [4]. The UPW cleaning procedure reduced the adventitious carbon levels. The XPS analysis resulted in a calculated carbon load of 76 to 151 ng/cm^2 for Al-6061 and 123 to 246 ng/cm^2 for SS-316L at a surface depth of 5 to 10 nm. XPS can not determine how much carbon is on the surface versus at depth. Mickelson [6] suggests the use of XPS calibration curves with known adventitious carbon layers in order to constrain AC versus particulate carbon and carbon at depth. If Mickelson's curves are used, they lower XPS-detected AC to a surface cleanliness of $< 20\text{ ng/cm}^2$ of C. The Raman analysis showed the Al-6061 surface had more adventitious carbon than the SS-316L. This could be indicative of more carbon uptake during the electropolishing process of the stainless steel.

Summary: Surface cleanliness classes such as IEST-STD-CC1246E for non-volatile residue (NVR) and ISO 14644-10 for chemical concentration are difficult to compare when the analytical technique can not detect adventitious carbon at XPS sensitivity. Consequently, surface contamination requirements for missions that do not specify a verification technique also complicate the cleanliness context. Future carbon contamination control requirements should account for adventitious carbon species on surfaces and employ multiple analytical techniques to fully characterize the surface cleanliness and contamination load. The reduction of adventitious carbon may require the use of cleaning techniques such as O_2 plasma or UV- O_3 treatment where the activated cleaned surface is never exposed to the atmospheric environment until astromaterials samples are collected [6].

Reference: [1] Castle, J.E. (2008) *J. of Adhesion*, 84:368-388; [2] Piao, H. et al. (2002) *Surface and Interface Analysis*, 22:591-594; [3] deVries, J.E. et al. (1994) *Ind. Eng. Chem. Res.*, 33:2618-2630; [4] Crist, B.V. (1999) *Handbook of the Elements and Native Oxide, XPS International*; [5] Kerber, S.J. et al. (2000) *Adv. Mat. & Processes*, Nov. [6] Mickelson, E.T. (2002) NASA JSC Doc. #29738.

Acknowledgements: Evans Analytical Group, Sunnyvale, CA were contracted by NASA JSC for XPS and Raman analyses of the test coupons.